

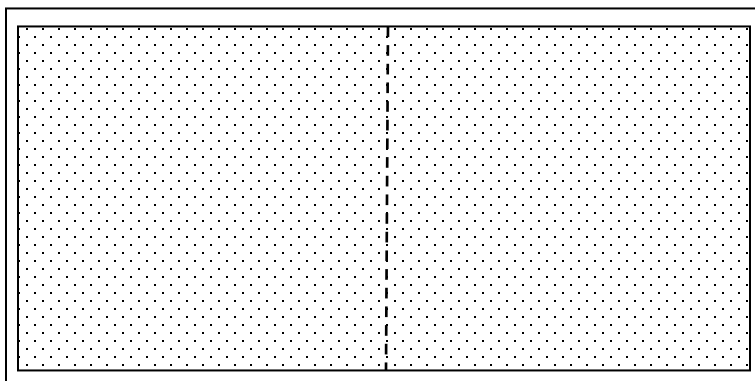
CHEM 371: Lecture 1

- What is time-dependent statistical mechanics?

As the name suggests, time-dependent statistical mechanics is a generalization of time-*independent* statistical mechanics in which time is an additional variable. But this generalization is not a simple matter of introducing time dependence into the various functions that appear in time-independent statistical mechanics, and we'll spend the rest of the lecture (and perhaps many more) trying to understand what it does entail. And to do that, we'll first need to recall some facts about time-independent statistical mechanics.

Broadly speaking, time-independent statistical mechanics is the study of the connection between the macroscopic properties of matter *in equilibrium* and the microscopic properties of its constituent elements. The operative words here are: *macroscopic*, *microscopic*, and *equilibrium*, and we'll need to be clear about what these words mean before moving on. We'll also need to be clear about the meaning of one other word that will come up in the discussion of the other three, and that is the word *average*. We can get a handle on all these terms by thinking about the behavior of a simple model system.

- So consider a gas of N independent *distinguishable* non-interacting particles enclosed in a sealed container under ambient conditions, and imagine mentally dividing the container into two equal halves. A snapshot of the particles in this arrangement might look like this:



where the dots represent the positions of individual gas particles. (You have to pretend that these dots are actually distributed *randomly* throughout the box.) Each of these particles is located in either the left half of the box or the right half. In one sense, then, every particle can be thought of as existing in just two states – left (L) or right (R).

If you now wanted to say something about the state of the gas at some instant of time (so that an interested third party could – in principle! – use the information to repeat what you were doing, for instance) you could do so at two levels: at one level, you could provide

an exhaustive list of the states of all N particles at some time t . Such a list might look like this:

$$1_L, 2_R, 3_R, 4_L, \dots, N_L$$

which says that the first particle is in the left half of the box, the second and third are on the right, the fourth is on the left, and so on.

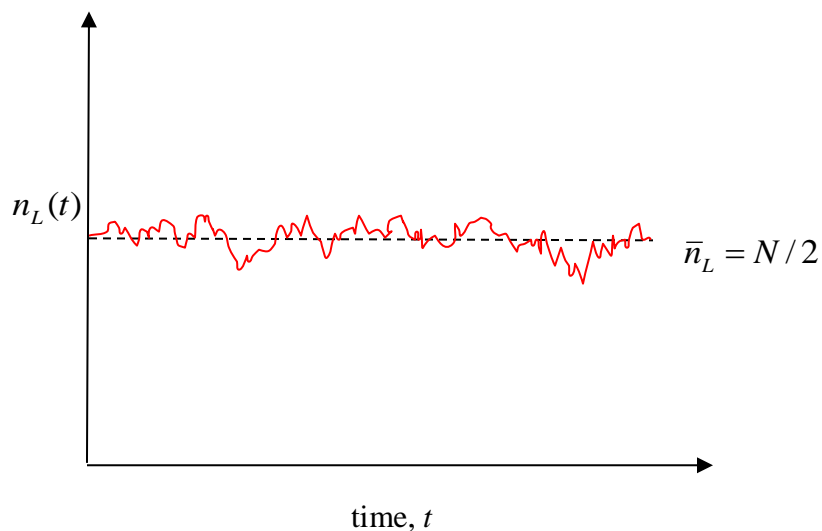
Alternatively, at another level, you could simply say how many of the particles were in the left half of the box, without indicating which particle was located where. At this level, your description of the state of the gas would consist of the value of just one variable, call it

$$n_L$$

the number of left-located particles.

The first level of description can be thought of as applying to the *microscopic* state of the gas, and the list of individual particle locations that characterize it can be thought of as a specification of the gas's *microstate*. The second level of description can be thought of as applying to the *macroscopic* state of the gas, and the single number n_L that characterizes it can be thought of as a specification of the gas's *macrostate*.

Both the microstate of the gas and its macrostate change with time because the particles are constantly moving from one side of the box to the other through collisions with themselves or with the walls of the box. But if N is very large (and it will be when moles of substance are involved), n_L will almost always be $N/2$, and its deviations from this value at different instants of time will be minuscule. A graph of n_L versus t would look something like this:



The value of $N/2$ around which n_L fluctuates (by tiny amounts!) is what we call the *time average* of n_L (which we'll denote \bar{n}_L), and this number, unlike n_L itself, is a constant, independent of time. It's because of this constancy in the average value of a variable that describes the gas's macrostate that we regard the gas as being in *equilibrium*. So for the moment, we'll define equilibrium as the condition of a system in which there's no change in the average values of its macroscopic variables (we'll refine this definition as we go along.)

- How do we actually determine average values? Experimentally, in the following way: by taking snapshots of the gas at a series of distinct times; making a note of the number of molecules in the left half of the box at these times; adding the numbers together and dividing by the number of snapshots. That is,

$$\bar{n}_L = \frac{n_L(t_1) + n_L(t_2) + \cdots + n_L(t_n)}{n} \approx \frac{N}{2}$$

If the time interval over which these measurements of particle number are made is large enough, and the intervals between successive measurements small enough, the sum in this expression can be replaced by an integral, and the average then effectively becomes

$$\bar{n}_L(t_0, \tau) = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} dt n_L(t)$$

where t_0 is the time at which the measurements are started and τ is the interval over they're made. The RHS of this equation is really only meaningful when τ is much greater than the time it takes for the system to rearrange itself. Ideally, we'd like τ to be infinitely large, in which case

$$\bar{n}_L(t_0) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} dt n_L(t)$$

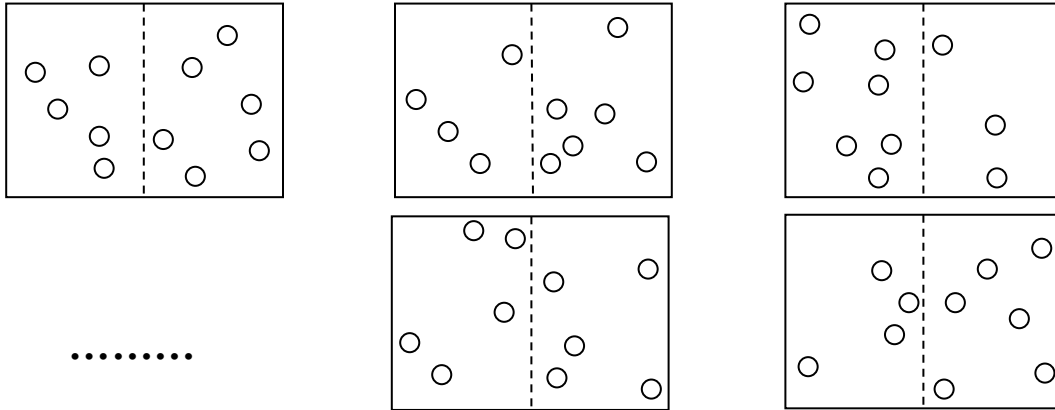
independent of τ . And if additionally, the system is in equilibrium (in the sense above), it won't matter when the measurement is started, and there's then no dependence on t_0 either, which can be set to 0. Hence,

$$\bar{n}_L = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt n_L(t)$$

- Time averages are what we tend to obtain automatically when we make experimental measurements of some macroscopic quantity because such measurements usually always take much, much longer than the time it takes for individual atoms or molecules to adopt

new configurations. During the course of an experimental measurement, in other words, the system will have had more than enough time to make numerous transitions between different microscopic arrangements.

We could have thought about this average somewhat differently. Instead of recording the values of $n_L(t)$ at separate instants of time, we could have started with a large collection, say, M , of distinct containers of the same gas, all of them prepared with the same number of molecules under the same *macroscopic* conditions, and each divided into two halves by an imaginary partition. At some common instant of time, the situation, pictorially, is like the one below for a gas of 10 molecules.



Some boxes have less than $N/2$ molecules in the left half, some have more, but if you added them together and divided by M , you'd expect the result to be approximately $N/2$, so long as both N and M were large. This way of calculating the average number of molecules in the left half of the box is called an *ensemble* average, and we'll denote it $\langle n_L \rangle$. So, in other words

$$\langle n_L \rangle = \frac{n_L^{(1)} + n_L^{(2)} + n_L^{(3)} + \cdots + n_L^{(M-1)} + n_L^{(M)}}{M}$$

We'll reformulate this definition shortly, but for now we'll regard the above expression as illustrative of the general procedure of ensemble averaging.

Ensemble averages are what we typically perform when we determine averages via statistical mechanics, and intuition suggests that there should be no difference between the time average of n_L and its ensemble average, and now we'll actually assert, as a **fundamental postulate** that

$$\bar{n}_L = \langle n_L \rangle \quad \text{(ergodic hypothesis)}$$

- Let's summarize what we've said up to this point. A macrostate of a system is defined by the set of properties that characterizes the system in the bulk, without reference to the atoms or molecules it's made up of. A microstate of the system is a specification of some property of every single atom or molecule in the system at some instant of time. Equilibrium is the condition of time independence of the macrostate. Experimental measurements of the variables of a system's macrostate yield time averages, while statistical mechanical estimates of the same quantities are usually obtained as ensemble averages.

- There's one important detail about macrostates and microstates that must be borne in mind: for any given macrostate of a system, there will in general be a large number of microstates that can give rise to it. In the example of the gas partitioned into two halves, for instance, a macrostate with $n_L = 4$, say, in a box with a total of 10 particles, could arise in $10!/(4! 6!) = 210$ ways. (The first particle to enter the left portion of the box could be any one of these 10 particles, the next could be any of the remaining 9, the third any of the remaining 8, and the fourth any of the remaining 7, for a total of $10 \times 9 \times 8 \times 7 = 5040$ possibilities; but since the order in which the 4 particles enter the left half is immaterial when determining n_L , 5040 has to be divided by the number of permutations of the labels on these particles, and that number is $4!$; 5040 divided by $4!$ is 210.)

The number of microstates that give rise to a given macrostate is called the multiplicity or the degeneracy of the macrostate, and it is usually denoted Ω . In a closed system (one isolated from the rest of the Universe), the entropy S and the multiplicity Ω are related by Boltzmann's famous equation

$$S = k_B \ln \Omega$$

Essentially all of equilibrium statistical mechanics is encapsulated in this one relation.

- The fact there can be many microstates for a given macrostate means that the ensemble average of a property like n_L can be written as

$$\langle n_L \rangle = \frac{\Omega_0 \times 0 + \Omega_1 \times 1 + \Omega_2 \times 2 + \cdots + \Omega_N \times N}{\Omega_0 + \Omega_1 + \Omega_2 + \cdots + \Omega_N}$$

where Ω_i is the degeneracy of a macrostate with i particles in the left of the box. The sum in the denominator is the total number of microstates available to this N -particle system, and if this number is denoted Ω , the ratio Ω_i/Ω can be interpreted as the probability p_i of observing a macrostate with $n_L = i \equiv n_L(i)$. This means that $\langle n_L \rangle$ can be written as

$$\langle n_L \rangle = \sum_{i=0}^N p_i n_L(i)$$

which is the form we will use subsequently in more general contexts.

● Digression: some terminology. We'll need to decide what properties must be specified to identify macro- and microstates unambiguously. To do that, it will help to make a quick detour into some terminology, so that we know precisely what we mean by certain terms that we'll use over and over again in statistical mechanical contexts. These terms may seem familiar, but they are to be understood in a definite way. Let's look at some of them: (see Castellan, *Physical Chemistry*.)

System. Any part of the physical universe we're interested in studying.

Surroundings. That part of the universe lying outside the system.

Boundary. The physical surface enclosing the system and separating it from the surroundings. Boundaries can be of several kinds:

- Rigid or moveable,
- Permeable (to matter flow) or impermeable or semi-permeable,
- Adiabatic (preventing heat flow) or diathermal (permitting heat flow).

Internal constraint. Any boundary within a system that divides it into two or more parts, called *sub-systems*. A system divided in this way into sub-systems is said to be *composite*. A system without internal constraints is said to be *simple*.

Closed system. One that is separated from the surroundings by a boundary that prevents any interaction between the two (Callen's definition; see his *Thermodynamics and an Introduction to Thermostatistics*). A closed system is completely isolated from its surroundings, and produces no observable effect or disturbance on it. (N.B. Other authors define a closed system as one in which no matter can pass through the boundary, though energy can, and an open system as one in which both energy and matter can pass through boundary.)

A system is said to have *properties*, which are those physical attributes that are perceived by the senses or can be made perceptible by certain methods of measurement. Different kinds of properties can be distinguished:

- Non-measurable, as the kinds of substances composing a system and the states of aggregation of its parts,
- measurable, to which a number can be assigned,
- *extensive*, which change in direct proportion to the size of the system,
- *intensive*, which are independent of the size of the system

A *phase* is a region within a simple system throughout which all of its properties are uniform.

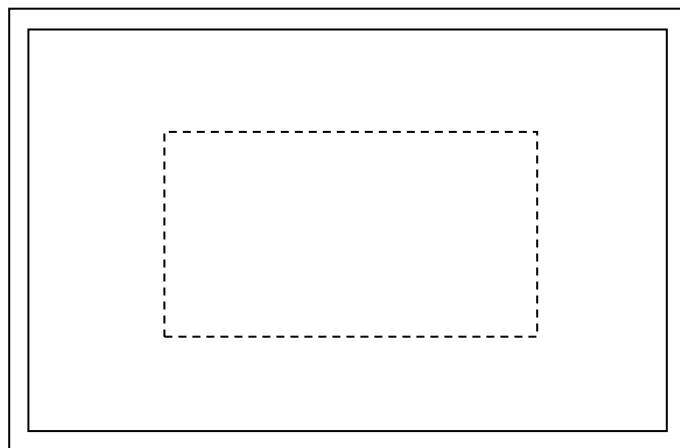
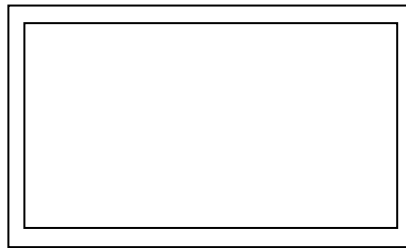
A system is said to be in a definite *state* when each of its properties has a definite value.

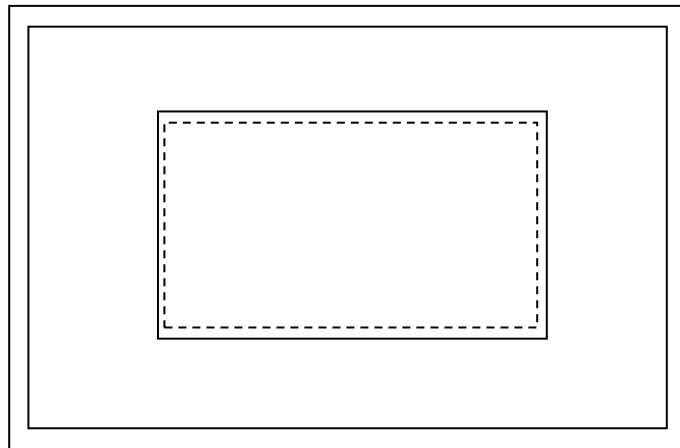
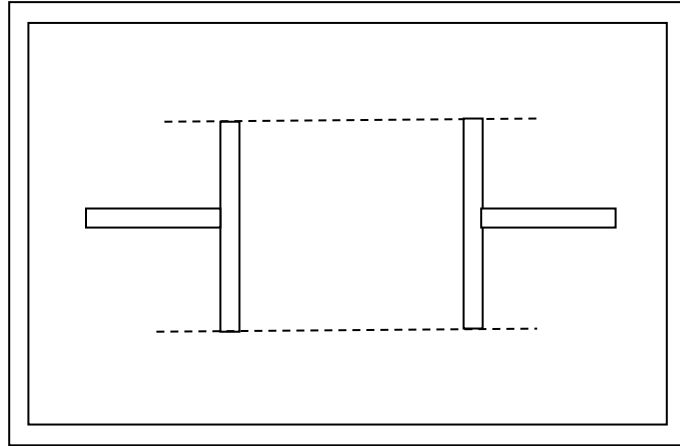
A change in state of a system occurs when at least one of its properties changes its value. The change in state is completely specified when the initial and final states are specified.

Systems initially in equilibrium will not change their state unless internal constraints are removed, or they are otherwise made to interact with their surroundings.

During a change of state, a system traverses a definite *path*, which is the ordered sequence of intermediate states lying between the initial and final states. If all the intermediate states in the path are equilibrium states, the path is said to be *quasi-static*. Physically, quasi-static means that if at any instant of time during the course of the change in state the system were isolated from its surroundings, all properties would be fixed at the values they had just prior to isolation. The path is said to be *reversible* if after a change of state, both system AND surroundings can be returned to their initial states. Reversible paths are idealizations, but can be approximated by quasi-static paths.

- With these preliminaries, we can start looking at more realistic situations than the one we considered for illustrative purposes. And the first thing we'd like to do is identify the variables that we think are sufficient to completely specify the state of a system at both the macroscopic and microscopic levels. For the moment, we'll restrict our attention to *classical* systems that are simple, that are not translating or rotating, and that are not subject to external fields. Such systems can be placed under a range of different conditions that are relevant to experiment. Here are some common possibilities, shown schematically





The first system is a *closed* system, completely isolated from its surroundings by a rigid, adiabatic, immovable boundary (the double lines). We'll state as a postulate (see Callen) that its macrostate is completely specified by U , V , N . (U is its internal energy – all the energy it possesses by virtue of the motion of molecules and their interactions with each other.)

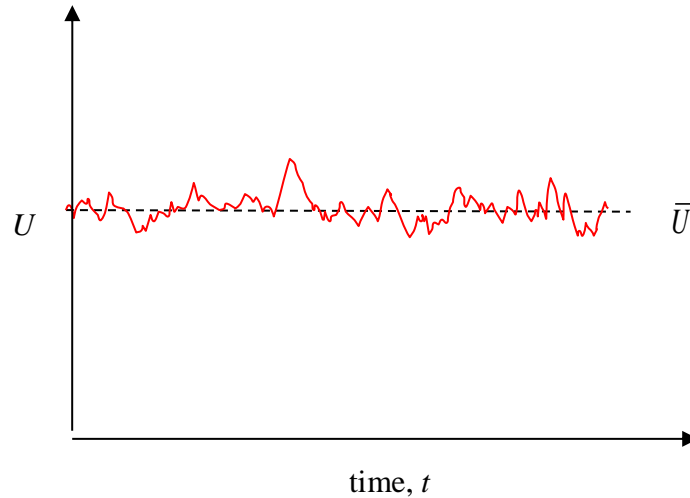
The second is a *closed composite* system. The system of interest is the inner container; it's assumed to interact with a heat bath or thermal reservoir. A heat bath is any system so large or so designed that no matter how much heat flows into or out it, its temperature T remains the same. Here, the system and reservoir are separated by a diathermal boundary, so heat flows freely between the two. The macrostate of the system is T , V and N .

The third is a *closed composite* system. The system of interest is the inner container; its surroundings constitute a temperature and pressure reservoir. A pressure reservoir is a system so large or so designed that no matter how much its volume changes, its pressure stays the same. (The atmosphere – under most conditions – is a pressure reservoir.) The

system and surroundings are separated by a diathermal, moveable boundary. The macrostate of the system is P, T, N .

The last is a *closed composite* system. The system of interest is the inner container; its surroundings constitute a temperature and particle reservoir. A particle reservoir is a system so large or so designed that no matter how many particles enter or leave it, its chemical potential remains the same. The system and surrounding are separated by a diathermal semi-permeable boundary. The macrostate state of the system is T, V, μ .

Apart from the first kind of system, which by itself is not very interesting since nothing happens to it, the others are slightly more complex realizations of our first illustrative example, in the following sense. Consider the system at T, V, N . Because the boundary is diathermal and energy U is freely exchanged between system and reservoir, the system has different amounts of energy at different instants of time, and a graph of U vs t would look like this:



As in the case of the gas, the variable U constantly changes from instant to instant, but the changes typically are very small if the system is large, and its average value, \bar{U} , obtained by adding up the energy values at different times and dividing by the number of measurements, is time-independent. Again, by virtue of this time independence of U (and the other macro variables), we say that the system is in equilibrium. An experimental measurement of U , because it takes longer than atomic/molecular timescales, is a time average of this variable.

A similar situation obtains for the system at constant T, V, μ . Now both energy and matter can flow across the boundary, which is diathermal and semi-permeable. So in this system, the macroscopic variables U and N fluctuate in time about an average value, which is the value that is recorded when that variable is measured physically, in a laboratory experiment. This average is time independent, and that being the case, the system is in equilibrium.

All of what we've just described refers to the macrostates of these systems. What about their microstates? We shall **postulate** that at the microscopic level, the system is completely specified by specifying the positions and momenta of every single particle in the system. If these variables are denoted q and p , we can now make the following identifications:

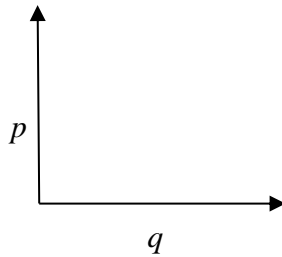
Macrostate: (U, V, N) or (T, V, N) or (T, P, N) .

Microstate: $\{q_1, p_1, q_2, p_2, \dots, q_N, p_N\}$

Macrostate: (T, V, μ)

Microstate: $\{q_1, p_1, q_2, p_2, \dots, q_i, p_i\}, \quad i = 1, 2, 3, \dots$

- Phase space. It's customary to think of these positions and momenta as spanning what we call a phase space, which for a collection of N particles in 3 dimensions is an abstract space made up of $6N$ mutually perpendicular axes, each axis corresponding to a particular Cartesian component of q or p for a particular particle. A point in this space is one possible microstate of the system. So, for example, if our system consisted of just a single particle in 1 dimension, its phase space would like this:



p and q are called phase space variables, and as a matter of notation, we'll use the symbol Γ to represent the collection of phase space variables that define a particular microstate. That is, $\{q_1, p_1, q_2, p_2, \dots, q_N, p_N\} \equiv \Gamma$. (In $3d$, the p 's and q 's become vectors.)

Quantities that we measure experimentally are in general functions of phase space variables, and we refer to them as *dynamical variables*. They are fundamentally mechanical (as opposed to statistical, like a distribution), and they depend, in general on time, because the p 's and q 's depend on time. So if A denotes the dynamical variable in question, we have

$$A(\Gamma(t)) = A(q_1(t), p_1(t), \dots, q_N(t), p_N(t))$$

which for notational simplicity we often simply write as $A(t)$.

Examples of dynamical variables:

- Velocity of i th particle, \mathbf{v}_i
- Kinetic energy, or potential energy, or total energy
- Distance between particles i and j , $|\mathbf{r}_i - \mathbf{r}_j|$
- Density of particles at some point, $\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$